

## ALUMINIUM ELECTROWINNING CELLS WITH METAL-BASED ANODES

Field of the Invention

This invention relates to aluminium electrowinning cells having metal-based anodes which contain at least one of nickel, iron and copper and which during use are inhibited from passivating and dissolving and from causing unacceptable contamination of the product aluminium.

Background Art

The technology for the production of aluminium by the electrolysis of alumina, dissolved in molten cryolite, at temperatures around 950°C is more than one hundred years old and still uses carbon anodes and cathodes.

Using metal anodes in commercial aluminium electrowinning cells would drastically improve the aluminium process by reducing pollution and the cost of aluminium production.

US Patents 4,614,569 (Duruz/Derivaz/Debely/Adorian), 4,680,094 (Duruz), 4,683,037 (Duruz) and 4,966,674 (Bannochie/Sheriff) describe non-carbon anodes for aluminium electrowinning coated with a protective coating of cerium oxyfluoride, formed in-situ in the cell or pre-applied, this coating being maintained by the addition of a cerium compound to the molten cryolite electrolyte. This made it possible to have a protection of the anode surface from the electrolyte attack and to a certain extent from the gaseous oxygen but not from the nascent monoatomic oxygen.

EP Patent application 0 306 100 (Nguyen/Lazouni/Doan) describes anodes composed of a chromium, nickel, cobalt and/or iron based substrate covered with an oxygen barrier layer and a ceramic coating of nickel, copper and/or manganese oxide which may be further covered with an in-situ formed protective cerium oxyfluoride layer. Likewise, US Patents 5,069,771, 4,960,494 and 4,956,068 (all Nguyen/Lazouni/Doan)

disclose aluminium production anodes with an oxidised copper-nickel surface on an alloy substrate with a protective oxygen barrier layer. However, full protection of the alloy substrate was difficult to achieve.

US Patent 6,248,227 (de Nora/Duruz) discloses an aluminium electrowinning anode having a metallic anode body which can be made of various alloys, for example a nickel-iron-copper alloy. During use, the surface of the anode body is oxidised by anodically evolved oxygen to form an integral electrochemically active oxide-based surface layer. The oxidation rate of the anode body is equal to the rate of dissolution of the surface layer into the electrolyte. This oxidation rate is controlled by the thickness and permeability of the surface layer which limits the diffusion of anodically evolved oxygen therethrough to the anode body.

US Patent 6,372,099 (Duruz/de Nora) discloses the use of transition metal species in an electrolyte below 910°C of an aluminium electrowinning cells to inhibit dissolution of metal-based anodes of the cell.

WO00/06803 (Duruz/de Nora/Crottaz) and WO00/06804 (Crottaz/Duruz) both disclose an anode produced from a nickel-iron alloy which is surface oxidised to form a coherent and adherent outer iron oxide-based layer whose surface is electrochemically active. WO00/06804 also mentions that the anode may be used in an electrolyte at a temperature of 820° to 870°C containing 23 to 26.5 weight%  $\text{AlF}_3$ , 3 to 5 weight%  $\text{Al}_2\text{O}_3$ , 1 to 2 weight%  $\text{LiF}$  and 1 to 2 weight%  $\text{MgF}_2$ .

US Patents 5,006,209 and 5,284,562 (both Beck/Brooks), 6,258,247 and 6,379,512 (both Brown/Brooks/Frizzle/Juric), 6,419,813 (Brown/Brooks/Frizzle) and 6,436,272 (Brown/Frizzle) all disclose the use of nickel-copper-iron anodes in an aluminium production electrolyte at 660°-800°C containing 6-26 weight%  $\text{NaF}$ , 7-33 weight%  $\text{KF}$ , 1-6 weight%  $\text{LiF}$  and 60-65 weight%  $\text{AlF}_3$ . The electrolyte may contain  $\text{Al}_2\text{O}_3$  in an amount of up to 30 weight%, in particular 5 to 10 or 15 weight%, most of which is in the form of suspended particles and some of which is dissolved in the electrolyte, i.e. typically 1 to 4 weight% dissolved  $\text{Al}_2\text{O}_3$ . In US Patents 6,258,247, 6,379,512, 6,419,813 and 6,436,272 such an electrolyte

is said to be useable at temperatures up to 900°C. In US Patents 6,258,247 and 6,379,512 the electrolyte further contains 0.004 to 0.2 weight% transition metal additives to facilitate alumina dissolution and improve cathodic operation.

US Patent 5,725,744 (de Nora/Duruz) discloses an aluminium production cell having anodes made of nickel, iron and/or copper in a electrolyte at a temperature from 680° to 880°C containing 42-63 weight%  $\text{AlF}_3$ , up to 48 weight%  $\text{NaF}$ , up to 48 weight%  $\text{LiF}$  and 1 to 5 weight%  $\text{Al}_2\text{O}_3$ .  $\text{MgF}_2$ ,  $\text{KF}$  and  $\text{CaF}_2$  are also mentioned as possible bath constituents.

Metal or metal-based anodes are highly desirable in aluminium electrowinning cells instead of carbon-based anodes. Many attempts were made to use metallic anodes for aluminium production, however they were never adopted by the aluminium industry for commercial aluminium production because their lifetime was too short and needs to be increased.

#### Summary of the Invention

One object of the invention is to provide an aluminium electrowinning cell incorporating metal-based anodes which remain substantially insoluble at the cell operating temperature and which can be operated without passivation or excessive contamination of the produced aluminium.

Another object of the invention is to provide an aluminium electrowinning cell operating with a crustless and ledgeless electrolyte, which can achieve high productivity, low contamination of the product aluminium, and whose components resist corrosion and wear.

The invention relates to a cell for electrowinning aluminium from alumina. The cell comprises: a metal-based anode having an outer part that contains at least one of nickel, cobalt and iron and that has an electrochemically active oxide-based surface; and a fluoride-containing molten electrolyte in which the active anode surface is immersed, the electrolyte being at a temperature below 950°C, in particular in the range from 910° to 940°C. The electrolyte consists of: 6.5 to 11 weight% of dissolved alumina; 35 to 44 weight%

aluminium fluoride; 38 to 46 weight% sodium fluoride; 2 to 15 weight% potassium fluoride; 0 to 5 weight% calcium fluoride; and 0 to 5 weight% in total of one or more further constituents.

5 For instance, the electrolyte consists of: 7 to 10 weight% dissolved alumina; 36 to 42 weight% aluminium fluoride, in particular 36 to 38 weight%; 39 to 43 weight% sodium fluoride; 3 to 10 weight% potassium fluoride, such as 5 to 7 weight%; 2 to 4 weight% calcium fluoride; and 0 to 3 weight% in total of one or more further constituents. This corresponds to a cryolite-based ( $\text{Na}_3\text{AlF}_6$ ) molten electrolyte containing an excess of aluminium fluoride ( $\text{AlF}_3$ ) that is in the range of about 8 to 15 weight% of the electrolyte, in particular about 8 to 10 weight%, and additives that can include potassium fluoride and calcium fluoride in the abovementioned amounts.

Such an electrolyte composition is well adapted for aluminium electrowinning at reduced temperature, i.e. at a temperature below the conventional aluminium electrowinning temperature of about 950°-970°C, using a metal-based anode containing at least one of nickel, cobalt and iron, usually in metallic and/or oxide form. The electrolyte is particularly adapted for anodes containing at least one of metallic nickel, metallic cobalt and oxides of iron. Oxides of iron include ferrous oxide, hematite, magnetite and ferrites (e.g. nickel ferrite), in stoichiometric and non-stoichiometric form. For example, the anode has a metallic alloy body that contains one or more of these metals - nickel, cobalt and iron - and that is covered with an integral active oxide layer or film.

The presence in the electrolyte of potassium fluoride in the given amount has two effects. On the one hand, it leads to a reduction of the operating temperature by up to several tens of degrees without increase of the electrolyte's aluminium fluoride content or even a reduction thereof compared to standard electrolytes operating at about 950°C with an aluminium fluoride content of about 45 weight%. On the other hand, it maintains a high solubility of alumina, i.e. up to above about 8 or 9 weight%, in the electrolyte even though the temperature of the electrolyte is reduced compared to conventional temperature.

Hence, in contrast to prior art low temperature electrolytes which carry large amounts of undissolved alumina in particulate form, according to the present invention a large amount of alumina in the electrolyte is in a dissolved form.

Without being bound to any theory, it is believed that combining a high concentration of dissolved alumina in the electrolyte and a limited concentration of aluminium fluoride leads predominantly to the formation of (basic) fluorine-poor aluminium oxyfluoride ions ( $[Al_2O_2F_4]^{2-}$ ) instead of (acid) fluorine-rich aluminium oxyfluoride ions ( $[Al_2OF_6]^{2-}$ ) near the anode. As opposed to acid fluorine-rich aluminium oxyfluoride ions, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate the anode's nickel and cobalt or dissolve the anode's iron. In particular, basic fluorine-poor aluminium oxyfluoride ions do not significantly passivate metallic nickel and cobalt, or dissolve iron oxides. The weight ratio of dissolved alumina/aluminium fluoride in the electrolyte should be above 1/7, and often above 1/6 or even above 1/5, to obtain a favourable ratio of the fluorine-poor aluminium oxyfluoride ions and the fluorine-rich aluminium oxyfluoride ions.

It follows, that the use of the above described electrolyte with metal-based anodes that contains at least one metal selected from nickel, cobalt and iron inhibits passivation and corrosion of said metal(s) of the anode, as demonstrated in the Examples below.

In order to maintain the alumina concentration above a given threshold in the abovementioned range during normal electrolysis, the cell is preferably fitted with means to monitor and adjust the electrolyte's alumina content.

Advantageously, the electrolyte contains on the active anode surface alumina at a concentration near saturation, typically above 80, 85 or even 90% of the alumina saturation concentration.

The abovementioned one or more further constituents of the electrolyte may comprise at least one fluoride selected from magnesium fluoride, lithium fluoride,

cesium fluoride, rubidium fluoride, strontium fluoride, barium fluoride and cerium fluoride.

Advantageously, the cell is sufficiently insulated to be operated with a substantially crustless and/or ledgeless electrolyte. Suitable cell insulation is disclosed in US patent 6,402,928 (de Nora/Sekhar), WO02/070784 and WO03/102274 (both de Nora/Berclaz).

The cell can have a cathode that has a aluminium-wettable surface, in particular a drained horizontal or inclined surface. Suitable cathode designs are for example disclosed in US Patents 5,683,559, 5,888,360, 6,093,304 (all de Nora), 6,258,246 (Duruz/de Nora), 6,358,393 (Berclaz/de Nora) and 6,436,273 (de Nora/Duruz), and in PCT publications WO99/02764 (de Nora/Duruz), WO00/63463 (de Nora), WO01/31086 (de Nora/Duruz), WO01/31088 (de Nora), WO02/070785 (de Nora), WO02/097168 (de Nora), WO02/097168 (de Nora), WO03/023091 (de Nora) and WO03/023092 (de Nora).

The cathode can have an aluminium-wettable coating that comprises a refractory boride and/or an aluminium-wetting oxide. Suitable aluminium-wettable materials are disclosed in WO01/42168 (de Nora/Duruz), WO01/42531 (Nguyen/Duruz/de Nora), WO02/070783 (de Nora), WO02/096830 (Duruz/Nguyen/de Nora) and WO02/096831 (Nguyen/de Nora).

The anode may have a metallic or cermet body and an oxide layer integral with or applied on the anode body.

Usually, the anode body is made from an iron alloy, in particular an alloy of iron with nickel and/or cobalt. Suitable alloys are disclosed in US Patent 6,248,227 (de Nora/Duruz) and in PCT publications WO00/06803 (Duruz/de Nora/Crottaz), WO00/06804 (Crottaz/Duruz), WO00/40783 (de Nora/Duruz), WO01/42534 (de Nora/Duruz), WO01/42536 (Duruz/Nguyen/de Nora), WO02/083991 (Nguyen/de Nora), WO03/014420 (Nguyen/Duruz/de Nora) and WO03/078695 (Nguyen/de Nora).

In one embodiment, the anode consists predominantly of iron and is optionally covered with an integral iron oxide-based layer.

For example, the anode body is made from an alloy consisting of:

- 65 to 95 weight% iron, in particular 75 to 90 weight%;
- 2 to 10 weight% aluminium, in particular 3 to 6 weight%;
- 0 to 5 weight% niobium, in particular 2 to 4 weight%;
- 5 - 0 to 3 weight% hafnium, in particular 1 to 2 weight%;
- 0 to 15 weight% in total of nickel and/or cobalt, in particular 0 to 10 or 0 to 6 weight%;
- 0 to 6 weight% copper, in particular 0 to 4 weight%;
- and
- 10 - 0 to 2 weight% in total of further constituents, in particular 0.5 to 1 weight%.

The total amount of niobium, hafnium and the abovementioned further constituents may be in the range from 0.25 to 3 weight%, in particular 0.75 to 2.5 weight%.

In another embodiment the anode body is made from a nickel and/or cobalt-based alloy.

- For example, the anode body is made from an alloy consisting of:
- 20 - 50 to 65% in total of nickel and/or cobalt, in particular 55 to 60 weight%;
  - 25 to 40 weight% iron, in particular 30 to 35 weight%;
  - 3 to 11 weight% copper, in particular 5 to 9 weight%;
  - 1 to 3 weight% aluminium, in particular 2 to 3 weight%;
  - 25 - 0 to 2 weight% niobium, in particular 0 to 1 weight%;
  - 0 to 2 weight% hafnium, in particular 0 to 1 weight%;
  - and
  - 0 to 2 weight% in total of further constituents, in particular 0.5 to 1 weight%.
  - 30

The total amount of niobium, hafnium and the abovementioned further constituents may be in the range from 0.25 to 5 weight%, in particular 1.5 to 3 weight%.

- Typically, the anode alloy is oxidised prior to or during use. This can lead to diffusion of metals in the anode, especially at the alloy's surface, which locally changes the alloy's composition.

- The anode body can be covered with an integral iron oxide-based layer containing oxides of iron and of at least one of nickel and cobalt, and optionally of one or more further metals, present in the following amounts calculated as weight% of the metals: 65 to 99 weight%

iron, in particular 80 to 95 weight%; 1 to 35 weight% in total of nickel and/or cobalt, in particular 5 to 20 weight%; and 0 to 3 weight% in total of said one or more further metals, in particular 0. to 1.5 weight%. Such  
5 integral layers are usually obtained by preoxidation of the body before and/or during use in the cell. However, integral oxide layers can also be obtained by in-situ oxidation.

The anode may also comprise an applied iron oxide-based coating. Suitable iron oxide-based coatings are  
10 disclosed in US Patents 6,361,681 (de Nora/Duruz), 6,365,018 (de Nora), 6,379,526 (de Nora/Duruz) and 6,413,406 (de Nora), and in PCT publication WO03/087435 (Nguyen/de Nora) and PCT applications PCT/IB03/03654,  
15 PCT/IB03/03978 (both Nguyen/de Nora) and PCT/IB03/05292 (Appourchaux/ Nguyen/de Nora). For example, the anode coating contains  $\text{Fe}_2\text{O}_3$  and optionally: at least one dopant selected from  $\text{TiO}_2$ ,  $\text{ZnO}$  and  $\text{CuO}$  and/or at least one inert material selected from nitrides and carbides.

Especially when used in the upper part of the  
20 abovementioned operating temperature range (e.g. 930°-950°C), the anode can comprise an applied cerium oxyfluoride-based outermost coating, for example as disclosed in the abovementioned US Patents 4,614,569,  
25 4,680,094, 4,683,037 and 4,966,674 or PCT Applications WO02/070786 (Nguyen/de Nora) and WO02/083990 (de Nora/Nguyen). Such a coating may be applied before or during use and maintained during use by the presence of cerium species in the electrolyte.

A stem, in particular containing nickel and/or  
30 iron, can be used to suspend the anode in the electrolyte. A suitable anode stem can have a core containing nickel and/or iron which is covered with an applied oxide coating, in particular an applied coating containing aluminium oxide and titanium oxide. The core  
35 of the stem can comprise a copper inner part and an outer part containing nickel and/or iron. Further details of anode stems are disclosed in PCT/IB03/02702 (Crottaz/Duruz).

Suitable anode designs are for example disclosed in  
40 WO99/02764 (de Nora/Duruz), WO00/40781, WO00/40782, WO03/006716, WO03/023091 and WO03/023092 (all de Nora).



Usually, the cell comprises at least one component, e.g. the cathode, that contains a sodium-active cathodic material, such as elemental carbon. This sodium-active cathodic material is preferably shielded from the electrolyte by a sodium-inert layer to inhibit the presence in the molten electrolyte of soluble cathodically-produced sodium metal that constitutes an agent for dissolving the active oxide-based anode surface. This mechanism is explained in greater detail in WO03/083176 (de Nora/Duruz).

The invention also relates to a cell that comprises:

- a metal-based anode having an outer part that has an electrochemically active oxide-based surface and that is made from an alloy consisting of:
  - 75 to 90 weight% iron;
  - 3 to 6 weight% aluminium;
  - 0 to 4 weight% in total of niobium and/or hafnium;
  - 0 to 10 weight% in total of nickel and/or cobalt;
  - 0 to 4 weight% copper; and
  - 0.5 to 1 weight% in total of further constituents;
- or
  - 55 to 60 weight % in total of nickel and/or cobalt;
  - 30 to 35 weight% iron;
  - 5 to 9 weight% copper;
  - 2 to 3 weight% aluminium;
  - 0 to 1 weight% in total of niobium and/or hafnium; and
  - 0.5 to 1 weight% in total of further constituents;
- an anode stem containing nickel and/or iron for suspending the anode in the electrolyte, the stem being covered with a coating of aluminium oxide and titanium oxide;
- a fluoride-containing molten electrolyte in which the active anode surface is immersed and which is at a temperature in the range from 910° to 940°C and which consists of: 7 to 10 weight% dissolved alumina; 36 to 42 weight% aluminium fluoride; 39 to 43 weight% sodium fluoride; 3 to 10 weight% potassium fluoride, such as 3 to 5 or 7 weight%; 2 to 4 weight% calcium fluoride; and 0 to 3 weight% in total of one or more further constituents; and
- a cathode having an aluminium-wettable surface, in particular a drained horizontal or inclined surface, formed by an aluminium-wettable coating of refractory hard material and/or aluminium-wetting oxide.

- A further aspect of the invention relates to a method of electrowinning aluminium in a cell as described above. The method comprises electrolysis of the dissolved alumina to produce oxygen on the anode and aluminium cathodically, and supplying alumina to the electrolyte to maintain therein a concentration of dissolved alumina of 6.5 to 11 weight%, in particular 7 to 10 weight%.

#### Brief Description of Drawings

- 10 The invention will be further described with reference to the accompanying drawings, in which:
- Figures 1a and 1b schematically show respectively a side elevation and a plan view of an anode for use in a cell according to the invention;
  - 15 - Figures 2a and 2b show a schematic cross-sectional view and a plan view, respectively, of an aluminium production cell for equipment with a potassium fluoride-containing electrolyte and a metal-based anode according to the invention; and
  - 20 - Figure 3 shows a schematic cross-sectional view of another aluminium production cell for equipment with a potassium fluoride-containing electrolyte and a metal-based anode according to the invention.

#### Detailed Description

- 25 Figures 1a and 1b schematically show an anode 10 which can be used in a cell for the electrowinning of aluminium according to the invention.

The anode 10 comprises a series of elongated straight anode members 15 connected to a cast or  
30 profiled support 14 for connection to a positive bus bar.

- The cast or profiled support 14 comprises a lower horizontally extending foot 14a for electrically and mechanically connecting the anode members 15, a stem 14b  
35 for connecting the anode 10 to a positive bus bar and a pair of lateral reinforcement flanges 14c between the foot 14a and stem 14b.

The anode members 15 may be secured by force-fitting or welding the foot 14a on flats 15c of the anode members 15. As an alternative, the connection between the anode members 15 and the corresponding receiving slots in the foot 14a may be shaped, for instance like dovetail joints, to allow only longitudinal movements of the anode members.

The anode members 15 have a bottom part 15a which has a substantially rectangular cross-section with a constant width over its height and which is extended upwardly by a tapered top part 15b with a generally triangular cross-section. Each anode member 15 has a flat lower oxide surface 16 that is electrochemically active for the anodic evolution of oxygen during operation of the cell. Also, the anode may be covered with a coating of iron oxide-based material, for example applied from a composition as set out in Table 3 below, and/or a coating of one or more cerium compounds in particular cerium oxyfluoride.

The anode members 15, in particular their bottom parts 15a, are made of an alloy comprising iron, nickel and/or cobalt as disclosed in Table 2 below. The lifetime of the anode may be increased by a protective coating made of cerium compounds, in particular cerium oxyfluoride as discussed above.

The anode members 15 are in the form of parallel rods in a coplanar arrangement, laterally spaced apart from one another by inter-member gaps 17. The inter-member gaps 17 constitute flow-through openings for the circulation of electrolyte and the escape of anodically-evolved gas released at the electrochemically active surfaces 16.

Figure 2a and 2b show an aluminium electrowinning cell having a series of metal-based anodes 10 in a fluoride-containing cryolite-based molten electrolyte 5 containing dissolved alumina according to the invention.

The electrolyte 5 has a composition that is selected from Table 1 below. The metal-based anodes 10 have a composition selected from Table 2 below, optionally with a protective coating made of cerium compounds, in particular cerium oxyfluoride as discussed above.

The anodes 10 are similar to the anode shown in Figs. 1a and 1b. Suitable alternative anode designs are disclosed in the abovementioned references.

5       The drained cathode surface 20 is formed by tiles 21A which have their upper face coated with an aluminium-wettable layer. Each anode 10 faces a corresponding tile 21A. Suitable tiles are disclosed in greater detail in WO02/096830 (Duruz/Nguyen/de Nora).

10       Tiles 21A are placed on upper aluminium-wettable faces 22 of a series of carbon cathode blocks 25 extending in pairs arranged end-to-end across the cell. As shown in Figures 2a and 2b, pairs of tiles 21A are spaced apart to form aluminium collection channels 36 that communicate with a central aluminium collection  
15       groove 30.

      The central aluminium collection groove 30 is located in or between pairs of cathode blocks 25 arranged end-to-end across the cell. The tiles 21A preferably cover a part of the groove 30 to maximise the  
20       surface area of the aluminium-wettable cathode surface 20.

      As explained hereafter, the cell is thermally sufficiently insulated to enable ledgeless and crustless operation.

25       The cell comprises sidewalls 40 made of an outer layer of insulating refractory bricks and an inner layer of carbonaceous material exposed to molten electrolyte 5 and to the environment thereabove. These sidewalls 40 are protected against the molten electrolyte 5 and the  
30       environment thereabove with tiles 21B of the same type as tiles 21A. The cathode blocks 25 are connected to the sidewalls 40 by a peripheral wedge 41 which is resistant to the molten electrolyte 5.

      Furthermore, the cell is fitted with an insulating  
35       cover 45 above the electrolyte 5. This cover inhibits heat loss and maintains the surface of the electrolyte in a molten state. Further details of suitable covers are disclosed in the abovementioned references.

40       In operation of the cell illustrated in Figs. 2a and 2b, alumina dissolved in the molten electrolyte 5 at a temperature of 880° to 940°C is electrolysed between

the anodes 10 and the cathode surface 20 to produce gas on the operative anodes surfaces 16 and molten aluminium on the aluminium-wettable drained cathode tiles 21A.

As demonstrated in the Examples below, corrosion and oxidation of anodes 10 used in electrolyte 5 is inhibited during operation.

The cathodically-produced molten aluminium flows on the drained cathode surface 20 into the aluminium collection channels 36 and then into the central aluminium collection groove 30 for subsequent tapping.

The cell shown in Figure 3 comprises a plurality of metal-based anodes 10 dipping in a molten electrolyte 5 according to the invention.

The anodes 10 are similar to the anode shown in Figs. 1a and 1b. Suitable alternative anode designs are disclosed in the abovementioned references.

The cell bottom comprises a series of pairs of spaced apart carbon cathode blocks 25 placed across the cell and having an aluminium-wettable upper surface 22 formed by an aluminium-wettable layer. The upper surfaces 22 are covered with aluminium-wettable openly porous plates 21 which are filled with molten aluminium to form an aluminium-wetted drained active cathode surface 20 above the upper surfaces 22 of the carbon cathode blocks 25. Further details of such a cathode bottom are disclosed in WO02/097168 and WO02/097169 (both de Nora).

The cathode blocks 25 are made of graphite and have a reduced height, e.g. 30 cm, and are coated with an aluminium-wettable layer which forms the upper surface 22 and which protects the graphite from erosion and wear. Suitable aluminium-wettable layers are disclosed in US Patent 5,651,874, WO98/17842, WO01/42168 and WO01/42531. The aluminium-wettable openly porous plates 21 covering the coated cathode blocks 25 can be made of the material disclosed in WO02/070783 (de Nora).

The cell bottom further comprises a centrally-located recess 35 which extends at a level below the upper surfaces 22 of the carbon cathode blocks 25 and which during use collects molten aluminium 60 drained

from the aluminium-wettable drained active cathode surface 20.

5 The aluminium collection recess 35 is formed in a reservoir body 30 which is placed between the blocks 25 of each pair of cathode blocks and spaces them apart across the cell. As shown in Figure 3, the recess 35 formed in the reservoir body 30 is generally U-shaped with rounded lower corners and an outwardly curved upper part.

10 The reservoir body 30 is made of two generally L-shaped sections 31 assembled across the cell. The reservoir sections 31 are made of anthracite-based material. The aluminium-wettable layer forming the upper surfaces 22 extends in the recess 35 to protect the reservoir body 30 during use against wear and sodium or potassium intercalation.

As shown in Figure 3, the reservoir body 30 extends below the cathode blocks 25 into the refractory and insulating material 26 of the cell bottom permitting 20 maximisation of the capacity of the aluminium collection recess 35.

Furthermore, the reservoir body 30 has a solid base 32 which extends from above to below the bottom face of the cathode blocks 25 and provides sufficient mechanical 25 resistance to keep the blocks 25 properly spaced apart across the cell when exposed to thermal expansion during start-up of the cell and normal operation. As shown in dotted lines in the upper part of the reservoir body 30, longitudinally spaced apart spacer bars 33 placed across 30 the reservoir body 30 may provide additional mechanical strength to the reservoir body 30. Such spacer bars 33 can be made of carbon material coated with an aluminium-wettable protective layer.

The openly porous plates 21 placed on the upper 35 surfaces 22 of the carbon cathode blocks 25 and located in the central region of the cell bottom extend over part of the aluminium collection recess 35 so that during use the protruding part of the aluminium-wetted drained active cathode surface 20 is located over the recess 35. 40

The openly porous plates 21 are spaced apart over the aluminium collection recess 35 to leave an access

for the tapping of molten aluminium 60 through a conventional tapping tube. The spacing between the openly porous plates 21 over the aluminium collection recess 35 can be much smaller along the remaining parts of the recess 35, thereby maximising the surface area of the active cathode surface 20.

The cell shown in Figure 3 comprises a series of corner pieces 41 made of the same openly porous material as plates 21 and filled with aluminium and placed at the periphery of the cell bottom against sidewalls 40. The sidewalls 40 and the surface of the electrolyte 5 are covered with a ledge and a small crust of frozen electrolyte 6. The cell is fitted with an insulating cover 45 above the electrolyte crust 6. Further details of suitable covers are disclosed in the abovementioned references.

The cell is also provided with exhaust pipes (not shown) that extend through the cover 45 for the removal of gases produced during electrolysis.

The cell comprises alumina feeders 50 with feeding tubes 51 that extend through the insulating cover 45 between the anodes 10. The alumina feeders 50 are associated with a crust breaker (not shown) for breaking the crust 6 underlying the feeding tube 51 prior to feeding.

In a variation, the insulating material of the sidewalls 40 and cover 45 may be sufficient to prevent formation of any ledge and crust of frozen electrolyte. In such a case, the sidewalls 40 are preferably completely shielded from the molten electrolyte 5 like in the cell of Figs. 2a and 2b or by a lining of the aforesaid openly porous material filled with aluminium.

Enhanced alumina dissolution may be achieved by utilising an alumina feed device which sprays and distributes alumina particles over a large area of the surface of the molten electrolyte 5. Suitable alumina feed devices are disclosed in WO00/63464 (de Nora/Berclaz) and in WO03/006717 (Berclaz/Duruz). Furthermore, the cell may comprise means (not shown) to promote circulation of the electrolyte 5 from and to the anode-cathode gap to enhance alumina dissolution in the electrolyte 5 and to maintain in permanence a high

concentration of dissolved alumina close to the active surfaces of anodes 10, for example as disclosed in WO00/40781 (de Nora).

During operation of the cell shown in Figure 3, alumina dissolved in the electrolyte 5 is electrolysed to produce oxygen on the anodes 10 and aluminium 60 on the drained cathode surfaces 20. The product aluminium 60 drains from the cathode surfaces 20 over the openly porous plates 21 that extend over part of the reservoir 30 into the reservoir 30 from where it can be tapped.

Hence, aluminium is produced on the drained active cathode surface 20 which covers not only the cathode blocks 25 but also part of the reservoir 30, thereby maximising the useful aluminium production area (i.e. the drained cathode surface 22) of the cell.

Corrosion and oxidation of anodes 10 used in electrolyte 5 is inhibited during operation, as demonstrated in the Examples below.

Figs. 2a, 2b and 3 show specific aluminium electrowinning cells by way of example. It is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art.

For instance the cell may have a sloping cathode bottom, as disclosed in WO99/02764 (de Nora/Duruz), and optionally one or more aluminium collection reservoirs across the cell, each intersecting the collection groove to divide the drained cathode surface into four quadrants as described in WO00/63463 (de Nora).

Examples of electrolyte compositions according to the invention are given in Table 1, which shows the weight percentages of the indicated constituents for each specimen electrolyte Al-II at a given temperature.



TABLE 1

	AlF <sub>3</sub>	NaF	KF	CaF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	T°C
A1	41	45	2.5	2.5	9	948°
B1	39.2	43.8	5	2	10	945°
C1	40.4	44.1	4	2	9.5	940°
D1	39.6	42.9	5	3	9.5	935°
E1	39	41.5	6.5	3.5	9.5	930°
F1	42	42	5	2	9	925°
G1	41.5	41.5	5	3	9	915°
H1	36	40	10	4	10	910°
I1	34	39	13	4	10	900°

5        Examples of alloy compositions of suitable metal-based anode are given in Table 2 that shows the weight percentages of the indicated metals for each specimen alloy A2-P2, in which specimens A2-I2 are nickel and/or cobalt-based alloys and specimens J2-P2 consist  
10        predominantly of iron.

TABLE 2

	Ni	Co	Fe	Cu	Al	Nb	Hf	other
A2	57	-	31	9	2	-	-	1
B2	55	-	33	9	2	-	-	1
C2	60	-	30	7.5	1.5	-	-	1
D2	25	35	32	5.5	1.5	-	-	1
E2	-	64	30	4	1.5	-	-	0.5
F2	15	45	28	9	2.5	-	-	0.5
G2	52	-	38	6	2	-	1.5	0.5
H2	12	50	26	8	1.5	1	1	0.5
I2	52	-	34	10	2	0.5	0.5	1
J2	3	-	91	-	5.5	-	-	0.5
K2	3	3	88	-	4	1.5	-	0.5
L2	10	-	80	1	6	1	1	1
M2	8	6	77	-	6	0.5	1.5	1
N2	-	14	72	5	6	2	-	1
O2	12	-	74	4	7	1	1.5	0.5
P2	6	3.5	80	2	4	3.5	-	1

5 The "other" elements refer to minor additives such as manganese, silicon and yttrium which may be present in individual amounts of 0.2 to 1.5 weight%. Usual impurities, such as carbon, have not been listed in Table 2.

10 Usually, these alloys will be surface oxidised before use and further oxidised during use, as described in the Examples below.

Examples of starting compositions of particle mixtures for producing hematite-based protective anode

coatings are given in Table 3, which shows the weight percentages of the indicated constituents for each specimen starting composition of the coating A3-L3.

TABLE 3

5

	Fe <sub>2</sub> O <sub>3</sub>	BN	AlN	ZrC	TiO <sub>2</sub>	ZrO <sub>2</sub>	ZnO	Ta <sub>2</sub> O <sub>5</sub>	CuO
A3	78	10	--	--	10	--	--	--	2
B3	78	10	--	--	--	--	10	--	2
C3	70	18	--	--	--	--	10	--	2
D3	78	10	--	--	--	10	--	--	2
E3	80	10	--	--	--	--	--	--	10
F3	78	10	--	--	--	--	--	10	2
G3	78	--	10	--	10	--	--	--	2
H3	78	--	12	--	--	--	5	3	2
I3	70	10	4	3	--	2	5.5	3	2.5
J3	75	14	--	--	5	5	--	--	1
K3	85	5	4	--	--	--	6	--	--
L3	75	--	--	12	5	--	--	5	3

#### Comparative Example 1

A metal-based anode was tested in a potassium fluoride-free electrolyte at 925°C.

- 10 The anode was manufactured from a rod of diameter 20 mm and total length 20 mm made from a cast nickel-based alloy having the composition of sample A2 of Table 2. The anode rod was supported by a stem made of an alloy containing nickel, chromium and iron, such as
- 15 Inconel, protected with an alumina sleeve. The anode was suspended for 16 hours over the molten fluoride-based electrolyte whereby its surface was oxidised prior to immersion into the electrolyte.

Electrolysis was carried out by fully immersing and polarising the anode rod in the molten electrolyte. The potassium fluoride-free electrolyte contained 45 weight% aluminium fluoride ( $\text{AlF}_3$ ), 45 weight% sodium fluoride ( $\text{NaF}$ ), 4 weight% calcium fluoride ( $\text{CaF}_2$ ) and 6 weight% alumina ( $\text{Al}_2\text{O}_3$ ). The saturation concentration of alumina in such an electrolyte, unattainable in practice, is at 7.6 weight%.

The current density was about  $0.8 \text{ A/cm}^2$  at the anode and the cell voltage was at 3.6-3.8 volt for 24 hours. The concentration of dissolved alumina in the electrolyte was maintained during the entire electrolysis by periodically feeding fresh alumina into the cell.

After 32 hours the cell voltage increased to 10 volt and electrolysis was interrupted. The anode was extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions had remained substantially unchanged. The anode's oxide outer part had grown from an initial thickness of about 20-30 micron to a thickness after use of about up to 1000 micron. A yellow-green layer of nickel fluoride ( $\text{NiF}_2$ ) was observed between the oxide outer part and the metallic inner part of the anode. Such a nickel fluoride layer is substantially non-conductive and passivates the anode, which caused the voltage increase.

Furthermore, a vermicular structure was observed in the metallic inner part immediately underneath the nickel fluoride layer over a depth of about 2 to 3 mm. The vermicular structure had mainly empty pores that had an average diameter of about 20 to 30 micron.

The aluminium produced during electrolysis was also analysed and showed a contamination by nickel of approximately 2500 ppm. This contamination was mainly caused by the dissolution of nickel from the anode's nickel-based alloy.

Comparative Example 2

The test carried out in Comparative Example 1 was repeated with an anode made from an iron-based alloy having the composition of sample L2 of Table 2.

- 5 During electrolysis the cell voltage increased progressively from about 3.6-3.8 volt to about 5 volt.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling, the anode was examined externally and in cross-section.

- 10 The anode's outer dimensions had not significantly changed. The anode's initial oxide outer part of about 100-150 micron thick had grown to a poorly adherent outer oxide scale of about 2-3 mm covering an adherent oxide layer of about 100 micron. It is believed that the  
15 poor adherence of the outer oxide scale on the adherent oxide layer caused the progressive voltage increase of the cell.

No vermicular structure was observed in the metallic inner part immediately underneath the oxide.

- 20 The aluminium produced during electrolysis was also analysed and showed a contamination by nickel of approximately 200 ppm.

Example 1

- A test was carried out with a cell according to the  
25 invention comprising: a molten potassium fluoride-containing electrolyte at 925°C having the composition of sample F1 of Table 1, i.e. rich in dissolved alumina, and an anode made from a nickel-iron alloy having the composition of sample A2 of Table 2.

- 30 The anode was manufactured like in Comparative Example 1 and suspended for 16 hours over the molten electrolyte.

- Electrolysis was carried out in the same potassium fluoride-containing electrolyte. The current density was  
35 about 0.8 A/cm<sup>2</sup> at the anode and the cell voltage was stable at 3.8 volt during the entire test. The dissolved

alumina-content was maintained around 9 weight% by periodically feeding fresh alumina into the cell.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions had remained substantially unchanged. The anode's oxide outer part had grown from an initial thickness of about 20-30 micron to a thickness after use of about up to 150 micron, instead of the 1000 micron observed in Comparative Example 1 (after only 32 hours electrolysis). Also, no passivating yellow-green layer of nickel fluoride ( $\text{NiF}_2$ ) was observed.

Immediately underneath the oxide outer part, a vermicular structure was observed in the metallic inner part over a depth of about 0.05 to 0.1 mm, instead of the 2 to 3 mm of Comparative Example 1. The vermicular structure had pores which were partly filled with oxides, in particular iron oxides, and which had an average diameter of about 2 to 5 micron.

The aluminium produced during electrolysis was also analysed and showed a contamination by nickel of approximately 1200-1500 ppm instead of the 2500 ppm of Comparative Example 1.

#### 25 Example 2

Example 1 was repeated with an anode made from the nickel-cobalt-iron alloy composition of sample D2 of Table 2 which was prepared, like in Example 1, over a potassium fluoride-containing electrolyte having the composition of sample F1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in Example 1 and showed similar results.

#### Example 3

35 Example 1 was repeated with an anode made from the iron-based alloy composition of sample L2 of Table 2 prepared, like in Example 1, over a potassium fluoride-

containing electrolyte having the composition of sample F1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in Example 1.

- 5 After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.

The anode's outer dimensions had remained substantially unchanged. The anode's oxide outer part had grown from an initial thickness of about 100-150  
10 micron to a thickness after use of about up to 500-700 micron, instead of the poorly adherent outer oxide scale of about 2-3 mm covering an adherent oxide layer of about 100 micron of Comparative Example 2.

- 15 No vermicular structure was observed in the metallic inner part.

The product aluminium had a low nickel contamination, i.e. less than 200 ppm nickel.

#### Example 4

- 20 Example 1 was repeated with an anode made from the nickel-iron alloy composition of sample A2 of Table 2 which was prepared, like in Example 1, over a potassium fluoride-containing electrolyte having the composition of sample D1 of Table 1, i.e. rich in dissolved alumina. The anode was then tested in the electrolyte like in  
25 Example 1 and showed similar results.

#### Example 5

- Examples 1 to 4 can be repeated using different combinations of electrolyte compositions (A1-I1) selected from Table 1 and anode alloy compositions (A2-P2) selected from Table 2.

#### Example 6

Another aluminium electrowinning anode was prepared as follows:

- 35 A slurry for coating an anode was prepared by suspending in 32.5 g of an aqueous solution containing 5 weight% polyvinyl alcohol (PVA) 67.5 g of a particle

mixture made of hematite  $\text{Fe}_2\text{O}_3$  particles, boron nitride particles,  $\text{TiO}_2$  particles and  $\text{CuO}$  particles (with particle size of -325 mesh, i.e. smaller than 44 micron) in a weight ratio corresponding to sample A3 of Table 3.

- 5        An anode made of the nickel-based alloy of sample A2 of Table 2 was covered with ten layers of this slurry that were applied with a brush. The applied layers were dried for 10 hours at  $140^\circ\text{C}$  in air and then consolidated at  $950^\circ\text{C}$  for 16 hours to form a protective hematite-based coating which had a thickness of 0.4 to 0.45 mm.

- 10       During consolidation, the  $\text{Fe}_2\text{O}_3$  particles were sintered together into a microporous matrix with a volume contraction. The  $\text{TiO}_2$  particles and  $\text{CuO}$  particles were dissolved in the sintered  $\text{Fe}_2\text{O}_3$ . The boron nitride  
15       particles remained substantially inert during the sintering but prevented migration and agglomeration of the micropores into cracks.

- Underneath the coating, an integral oxide scale mainly of iron oxide had grown from the anode's alloy  
20       during the heat treatment and combined with iron oxide and titanium oxide from the coating to firmly anchor the coating to the oxidised alloy. The integral oxide scale contained titanium oxide in an amount of about 10 metal weight%. Minor amounts of copper, aluminium and nickel  
25       were also found in the oxide scale (less than 5 metal weight% in total).

- Electrolysis was carried out in a potassium fluoride-containing electrolyte at  $925^\circ\text{C}$  having the composition of sample F1 of Table 1, i.e. rich in dissolved alumina. The current density was about 0.8  $\text{A}/\text{cm}^2$  at the anode and the cell voltage was stable at 3.6 volt during the entire test, instead of the 3.8 volt observed in Examples 1 to 4. The dissolved alumina-content was maintained around 9 weight% by periodically  
30       feeding fresh alumina into the cell.

After 50 hours electrolysis was interrupted and the anode extracted. Upon cooling the anode was examined externally and in cross-section.



The anode's outer dimensions as well as the anode's coating had remained substantially unchanged. However,  $\text{TiO}_2$  had selectively been dissolved in the electrolyte from the coating. The anode's structure underneath the coating was similar to the structure observed in Examples 1 to 4.

Samples of the used electrolyte and the product aluminium were also analysed. It was found that the electrolyte contained less than 70 ppm nickel and the produced aluminium contained less than 300 ppm nickel which is significantly lower than with an uncoated anode that can cause a typical nickel contamination of 1200-1500 ppm in the product aluminium.

#### Example 7

Example 6 can be repeated using different combinations of electrolyte compositions (A1-I1) selected from Table 1, anode alloy compositions (A2-P2) selected from Table 2 and coating compositions (A3-L3) selected from Table 3.

Further details on the application of such anode coatings and suitable compositions are disclosed in the abovementioned references.

In summary, as can be seen by comparing Example 1-5 to the Comparative Examples, using the potassium-fluoride electrolyte of the invention containing about 8 weight% dissolved alumina instead of a potassium-fluoride free electrolyte containing only 4 weight% dissolved alumina, inhibits fluorination and passivation of the nickel and/or cobalt of the anode and reduces wear (oxidation and dissolution of the anode's iron).

Furthermore, as can be observed from Examples 6-7, use of a crack-free nickel-free hematite-based protective coating on a nickel-iron anode alloy reduces the cell voltage and significantly inhibits contamination of the product aluminium by nickel from the anode, compared to an uncoated nickel-iron anode operated in the same type of electrolyte.